



## Short communication

## A novel polyquinone cathode material for rechargeable lithium batteries

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## HIGHLIGHTS

- We present a new organic quinone polymer, poly(5-amino-1,4-dihydroxy anthraquinone) (PADAQ).
- PADAQ shows low solubility in electrolyte and no crystallization during charge and discharge process.
- Analogous polyaniline structure makes for improving the conductivity of the materials.
- PADAQ is sensitive to discharge depth.
- The electrochemical reaction mechanism of PADAQ electrode is proposed.

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## ABSTRACT

A novel polymer, poly(5-amino-1,4-dihydroxy anthraquinone) (PADAQ) as the cathode material of lithium batteries is synthesized by a facile oxidation process and characterized by FT-IR, MS, elementary analysis, XRD, SEM and electrochemical method. The results show that the as-prepared polymer solves the problems of dissolution and crystallization of its monomer, 5-amino-1,4-dihydroxy anthraquinone (ADAQ), thus maintains the stability of the electrode structure successfully. At the cutoff voltage of 1.5–3.7 V, the initial discharge capacity of PADAQ is 101 mAh g<sup>-1</sup> at the current density of 400 mAh g<sup>-1</sup>. After 14 cycles, the capacity increases to 143 mAh g<sup>-1</sup>, and maintains 129 mAh g<sup>-1</sup> after 50 cycles, which shows an improved cycle performance compared to its monomer. Even at the high current density of 1400 mAh g<sup>-1</sup>, its capacity still reaches 95 mAh g<sup>-1</sup>, indicating a high rate capacity. The results also show that PADAQ is sensitive to discharge depth. When discharged to 1.0 V, its cycle performance is poor.

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## 1. Introduction

Energy can be considered as the lifeblood of our modern society. However, the widespread use of coal and petroleum doesn't meet the needs of the low-carbon economy and sustainable development. So a clean and sustainable energy supply is essential for the future of human beings. For energy storage and use, Lithium secondary batteries represent the promising power sources because of their advantages in energy density and cyclability. However, they still fall short of both the sustainability and CO<sub>2</sub> footprint criteria. The conventional cathode materials of lithium secondary batteries (e.g. LiCoO<sub>2</sub>, LiNiO<sub>2</sub>) are mostly obtained from limited mineral resources and synthesized by high temperature

reaction [1]. Furthermore, safety issues in lithium metal oxide cathodes are critical because of their intrinsic thermal properties, e.g. fully charge lithium cobalt oxide can release oxygen which oxidizes the solvent to cause the battery explosion [2]. Therefore, it is indispensable to develop the "green and sustainable" lithium batteries with higher safety, higher capacity and richer reserves in nature.

Compared with the conventional inorganic materials, the organic compounds as lithium batteries cathode materials have the advantages of higher theoretical specific capacity, abundance of raw materials, environmental friendliness, feasible structure designability and system safety [1,3]. Here, we are interested in organic compound quinones [3–12], which show preferable electrochemical reversibility [7,13–20]. Such as a lithiated quinone compound (Li<sub>2</sub>C<sub>6</sub>O<sub>6</sub>) [1], which was synthesized from a renewable resource (i.e. myo-inositol), showing a reversible capacity as high as 580 mAh g<sup>-1</sup>. However, the factual capacities of many quinone

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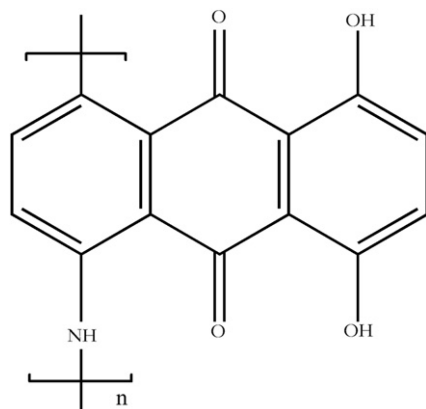


Fig. 1. The molecular structure of PADAQ.

compounds are much lower than their theoretical ones, and their capacities decrease seriously during cycling. The reasons are mainly that quinone compounds are easy to dissolve in organic electrolyte and crystallize during the discharge process, in addition, these materials are electrical insulators [5]. In order to solve these problems, we have prepared a parasitic mesoporous carbon/9,10-anthraquinone composite [21], in which the “parasitifer” carbon material with hierarchical porous structure, high electrical conductivity and high specific surface area played threefold roles: minimizing the size of quinone compound embedded in nanoporous, delivering electrons efficiently to the quinone compounds and trapping the soluble redox product. But the cycle capacity of this composite still decays apparently. New methods to improve the cycle performance are still in need.

In this paper, we present a new organic quinone polymer, poly(5-amino-1,4-dihydroxyanthraquinone) (PADAQ) which shows low solubility in electrolyte and no crystallization during charge and discharge process (Fig. 1).

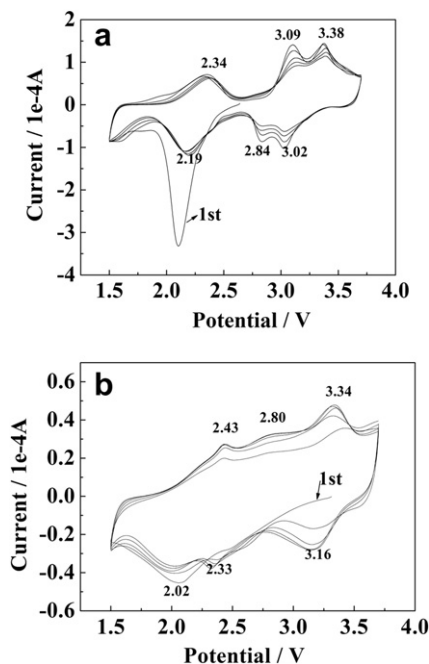


Fig. 2. CV curves of monomer ADAQ (a) and PADAQ (b) electrodes (conditions: cutoff voltage = 1.5–3.7 V, scan rate = 0.5 mV s<sup>-1</sup>).

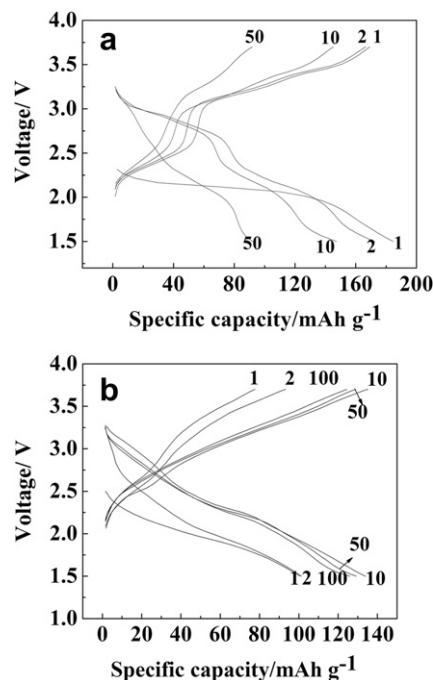


Fig. 3. The discharge and charge curves of monomer ADAQ (a) and PADAQ (b) electrodes (conditions: cutoff voltage = 1.5–3.7 V, current density = 400 mA g<sup>-1</sup>).

## 2. Experimental procedures

### 2.1. Synthesis and characterization of PADAQ

One gram of 5-amino-2,3-dihydro-1,4-dihydroxyanthraquinone (2.90 mmol) was dissolved in 50 ml of warm glacial acetic acid. A ca. 25% aqueous ammonium persulfate solution (5 ml) was added slowly and the resulting mixture was left stirring for 4 h at ice salt bath. The precipitate was then collected by filtration, thoroughly washed with water and dried under high vacuum to yield the desired polymer (PADAQ) as a reddish brown powder product (0.85 g). PADAQ: FT-IR (KBr),  $\nu$  (cm<sup>-1</sup>): 3429 (N–H stretch), 1719 (C=O), 1580 (C=C<sub>ar</sub> stretch), 1491 (N–H deformation), 1205 (C–N stretch), 835 (C–H out-of-plane bending vibration of 2H), 796 (C–H out-of-plane bending vibration of 3H). ADAQ: FT-IR (KBr),  $\nu$  (cm<sup>-1</sup>): 3470/3343 (N–H stretch), 1608 (C=O), 1540 (C=C<sub>ar</sub> stretch), 1460 (N–H deformation), 1227 (C–N stretch), 836 (C–H out-of-plane bending vibration of 2H), 782 (C–H out-of-plane bending vibration of 3H). Elemental analysis (%) Calcd. for M: C 65.88, H 3.55, N 5.49. Found: C 66.35, H 3.05, N 5.61. MALDI-TOF MS:  $m/z$  491.1 (2M<sup>+</sup> – 2OH), 522.7 (2M<sup>+</sup>), 761.3 (3M<sup>+</sup> – OH), 1014.4 (4M<sup>+</sup> – OH).

5-amino-1,4-dihydroxyanthraquinone (ADAQ) were synthesized by our group [22].

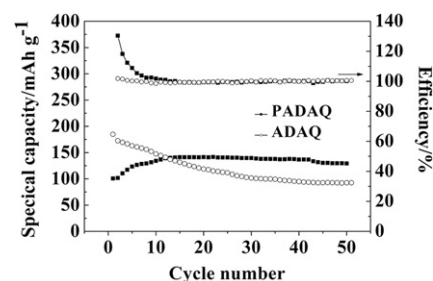


Fig. 4. Cycle performance of monomer ADAQ and PADAQ electrodes (current density = 400 mA g<sup>-1</sup>).

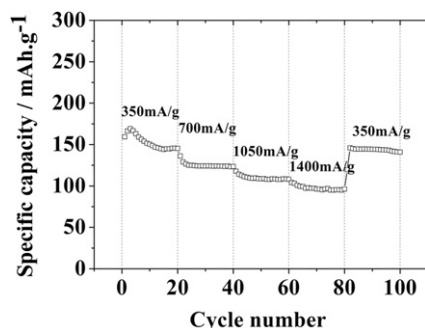


Fig. 5. Rate performance of PADAQ electrode.

## 2.2. Battery assembled

The positive electrode is comprised of 50 wt% PADAQ (or ADAQ), 40 wt% acetylene black, 10 wt% poly(vinylidene fluoride) binder. Lithium metal foil is used as the counter electrode. The cathode and lithium foil anode was separated by a Celgard 2400 membrane. An electrolyte solution of a 1.0 M  $\text{LiPF}_6$  in EC/DEC (1:1 by volume) is used. The simulated batteries are assembled in argon atmosphere glove box.

## 2.3. Instrument

FT-IR spectra are recorded on a NICOLET AVATAR 360 FT-IR spectrometer with KBr pellets. The morphology of PADAQ electrode is characterized by SEM performed on a FEI HITACHI 4800 microscope operated at 20 kV. Mass spectra are determined using a Hewlett–Packard Model 5988A mass-selective detector equipped with a Hewlett–Packard MS Chem Station. Elemental analysis (EA) of the sample is conducted on a VarioEL III element analysis instrument. XRD pattern is recorded on a Rigaku diffractometer using  $\text{Cu K}\alpha$  radiation in  $2\theta$  range of  $10^\circ$ – $80^\circ$ . The cyclic voltammetry (CV) (scan rate:  $0.5 \text{ mV s}^{-1}$ ) test is conducted with a Solartron 1280Z electrochemical workstation. The galvanostatic charge/discharge tests are performed

to evaluate the electrochemical capacity and cycle life of electrodes at room temperature under a LAND-BTI-10 instrument.

## 3. Results and discussion

### 3.1. Electrochemical performances of PADAQ

The cyclic voltammogram of monomer ADAQ and PADAQ electrodes are presented in Fig. 2. For monomer ADAQ, the CV curve shows three pairs of redox peaks, which should be attributed to the electrochemical reaction of hydroxyl and carbonyl groups. Two pairs of redox peaks of carbonyl groups are located at 2.84/3.09 V and 3.02/3.38 V, while a pair of redox peaks of hydroxyl groups appears at 2.19 and 2.34 V [23]. For PADAQ, the two pairs of redox peaks of carbonyl groups are located at 2.33/2.02 V and 2.43/2.80 V, while the redox peaks near 3.16 and 3.34 V is corresponding to the doping and undoping reaction of polymer chain, which is consistent with similar polymers, such as Poly(5-amino-1,4-naphthoquinone), Poly(1-aminoanthraquinone), Poly(1,5-diaminoanthraquinone) [9,24,25]. The results indicate that the hydroxyl groups of PADAQ don't participate in electrochemical reaction between 1.50 and 3.70 V. The variation between the voltammetry of ADAQ and PADAQ may be explained by introducing polyaniline chain.

The galvanostatic charge/discharge curves of the monomer ADAQ and PADAQ electrodes are shown in Fig. 3. It reveals that ADAQ has two voltage plateaus at about 2.3 V and 3.0 V, while PADAQ has no obvious voltage plateaus. The initial discharge curves of ADAQ and PADAQ show much lower voltage plateaus than the discharge curves of the followed cycle, which indicates electrochemical activation occurring through the first charge process. Fig. 4 displays the cycle performance of monomer ADAQ and PADAQ at current density of  $400 \text{ mA g}^{-1}$ . The coulomb efficiencies of ADAQ and PADAQ are always above 99% during the whole test. ADAQ shows a higher initial capacity of  $185 \text{ mAh g}^{-1}$ , but its capacity decay is severe, after 50 cycles, its specific capacity is only  $93 \text{ mAh g}^{-1}$ . For PADAQ, after 50 cycles, its specific capacity still remains  $129 \text{ mAh g}^{-1}$ , illustrating a better cycle performance than

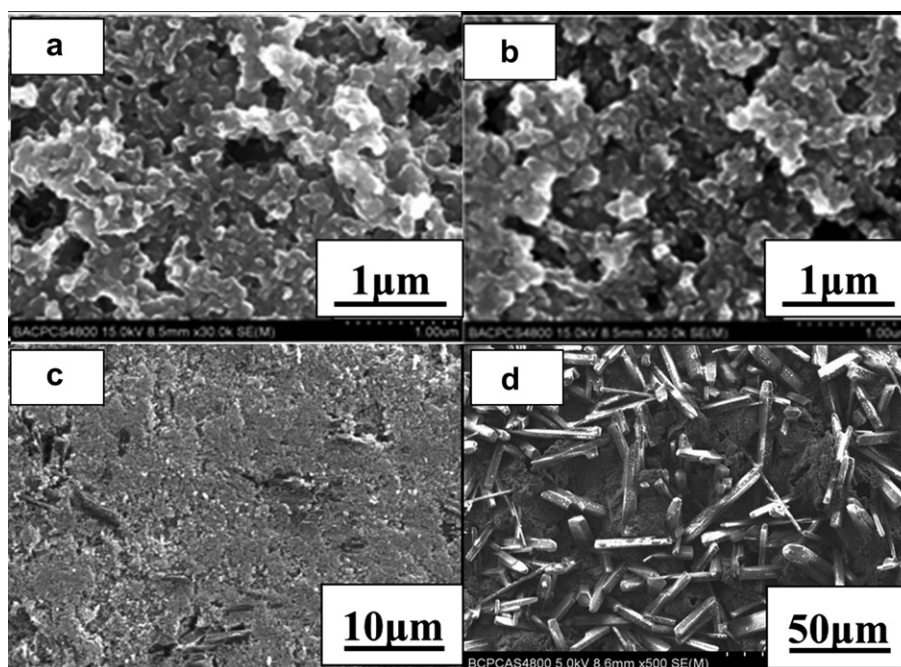


Fig. 6. SEM images of PADAQ electrode (a, original; b, after the 10th discharge) and ADAQ electrode (c, original; d, after the 10th discharge).

that of ADAQ. It is notable that the capacity of PADAQ gradually increases during the first 14 cycles. This phenomenon can be seen from the reports of conducting polymer, such as Polyimides [26], Poly(2,5-dihydroxy-1,4-benzoquinone-3,6-methylene) [27], which ascribes to the gradual increase amount of doping ions in the polymer chains.

In order to evaluate the rate performance of PADAQ, tests were carried out at current densities from  $350 \text{ mA g}^{-1}$  to  $1400 \text{ mA g}^{-1}$  and then back to  $350 \text{ mA g}^{-1}$ , and the results are shown in Fig. 5. From  $350 \text{ mA g}^{-1}$  to  $1400 \text{ mA g}^{-1}$ , the discharge capacity decreases from  $168 \text{ mAh g}^{-1}$  to  $95 \text{ mAh g}^{-1}$ , and when the current density gets back to  $350 \text{ mA g}^{-1}$ , the capacity quickly recovers to  $140 \text{ mAh g}^{-1}$ . This result demonstrates that the kinetics of the lithium/polyquinone redox reaction is fast and this electrochemistry system is suitable high power application.

### 3.2. Morphology and XRD analysis

In order to analyze the reasons for the excellent electrochemical performance of PADAQ electrode, the SEM images of PADAQ and ADAQ electrodes in the different discharge stage. The SEM images are illustrated in Fig. 6. For PADAQ, the morphology of electrode after the 10th discharge (Fig. 6b) shows no obvious changes compared with that of the original electrode (Fig. 6a). But for ADAQ, the morphology of electrode after the 10th discharge (Fig. 6d) changes obviously. A great deal of needle-like crystals appears at the surface of the electrode, which are lithium salt crystals formed through the intercalation reaction of lithium ions during discharge process. This process results in the separation between active material and conductive additives, which is the main reason for the severe capacity decay.

XRD patterns for ADAQ and PADAQ electrodes at original and after 10 cycles state are presented in Fig. 7. The original ADAQ electrode and after 10 cycles one show multiple peaks of varying intensity, indicating that both ADAQ and its discharge products have crystal structure. For the electrodes of PADAQ in two stages, only a broad peak centered at  $2\theta = 27^\circ$  appears at the XRD patterns respectively, which demonstrates the polymer has amorphous structure. This result is well consistent with the SEM analysis.

The solubility of PADAQ and ADAQ in their charge and discharge process was also compared. Fig. 8 shows the electrolytic cell photos of PADAQ and ADAQ after 10 cycles. The electrolyte of ADAQ presents a salmon pink color and that of PADAQ is almost colorless, which indicates that PADAQ and its discharge products are difficult to dissolve in the electrolyte. Accordingly, we can draw the conclusion that the polymer effectively solves the problems of dissolution and crystallization of its monomer with small molecule, thus maintains the structure of electrode stable, which is the main reason for its improved cycle performance.

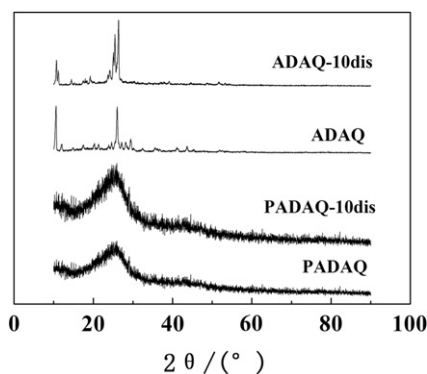


Fig. 7. XRD patterns of ADAQ, PADAQ electrodes at original and after 10 cycles state.

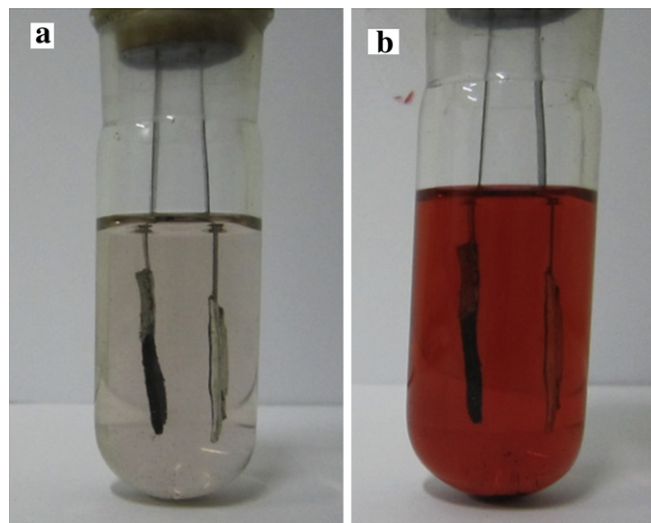


Fig. 8. The photos of PADAQ (a) and ADAQ (b) electrolytic cells after 10 cycles.

### 3.3. Electrochemical mechanism

The deep discharge tests were carried out between 1.0 and 3.7 V (Fig. 9) to discuss the influence factors to the capacity of PADAQ. When discharged to 1.0 V, the specific capacity of PADAQ reaches as high as  $322 \text{ mAh g}^{-1}$ , which is much higher than that of PADAQ when discharged to 1.5 V. It is notable that the discharge curves have a sloping plateau in the potential range of 1.5–1.0 V, resulting in the increase of specific capacity. The cycle performance of PADAQ at cutoff voltage of 1.0–3.7 V is showed in Fig. 9b. After 100 cycles, the specific capacity of PADAQ only remains  $135 \text{ mAh g}^{-1}$ , about 58% of the initial capacity, which shows an obvious deterioration on cycle performance compared to that of PADAQ at cutoff voltage of 1.5–3.7 V. This result demonstrates that PADAQ is sensitive to discharge depth. We tested the gas generated from the discharge

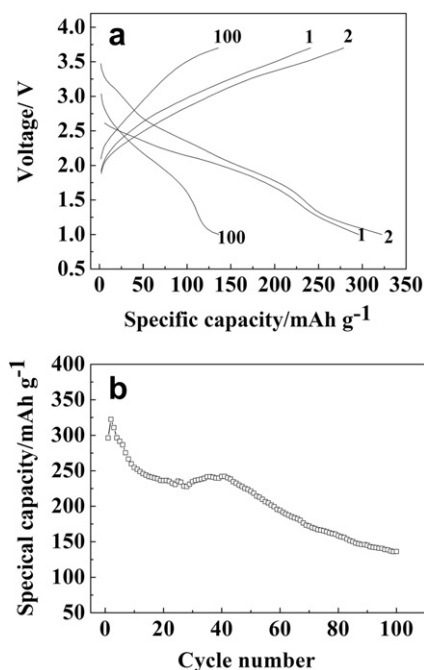
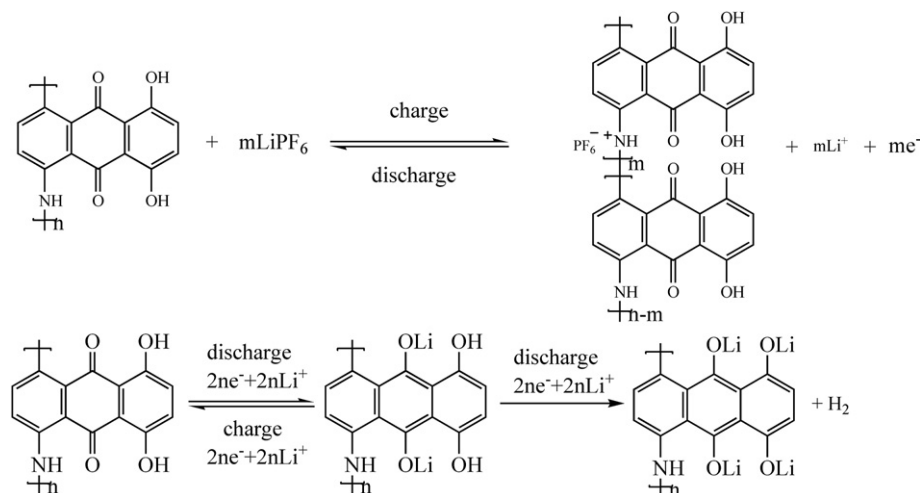


Fig. 9. The deep discharge and charge curves of PADAQ electrode (a) and cycle performance (b) (conditions: cutoff voltage = 1.0–3.7 V, current density =  $400 \text{ mA g}^{-1}$ ).





**Scheme 1.** The electrochemical mechanism scheme of PADAQ.

process by gas chromatography and proved the existence of hydrogen. So it can be surmised that the deterioration of cycle performance is related to the electrochemical reduction of hydroxyl groups of PADAQ, which is an irreversible process.

According to the above results, a scheme for the electrochemical reaction mechanism of PADAQ is proposed in **Scheme 1**. The doping and undoping reaction on analogous polyaniline chain happens between 3.7 and 3.3 V, and the carbonyl and hydroxyl groups participate in the electrochemical reaction at the voltage range of 3.3–1.5 V and 1.5–1.0 V, respectively.

#### 4. Conclusions

A novel polyquinone cathode material PADAQ was synthesized for the first time and its electrochemical performance was studied in this paper. The results show that at the cutoff voltage of 1.5–3.7 V, PADAQ possesses an initial capacity of 101 mAh g<sup>-1</sup> at current density of 400 mA g<sup>-1</sup>, after 14 cycles, its capacity increases to up 143 mAh g<sup>-1</sup>, and maintains 126 mAh g<sup>-1</sup> after 50 cycles; at high current density of 1400 mA g<sup>-1</sup>, the specific capacity of PADAQ still remains 95 mAh g<sup>-1</sup>, which demonstrates an excellent cyclability and rate performance. The reason for the improved electrochemical performance is that the polymer can fundamentally solve the problems of dissolution and crystallization of its monomer, thus can maintain the stable structure of electrode during the cycling process. When deeply discharged to 1.0 V, PADAQ shows a poor cycle performance, which might ascribe to the electrochemical reaction of hydroxyl groups in it.

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